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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>C23C 22/16</b>	<b>A1</b>	(11) International Publication Number: <b>WO 96/27693</b>
		(43) International Publication Date: 12 September 1996 (12.09.96)

(21) International Application Number: PCT/US96/02678

(22) International Filing Date: 5 March 1996 (05.03.96)

(30) Priority Data:  
7/47195 7 March 1995 (07.03.95) JP

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(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

**Published***With international search report.**Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*

(54) Title: COMPOSITION AND PROCESS FOR SIMULTANEOUSLY CLEANING AND CONVERSION COATING METAL SURFACES

## (57) Abstract

An oil- or grease-soiled metal surface can be simultaneously cleaned and phosphate conversion coated by contact with a zinc phosphating composition comprising surfactant, zinc ions, phosphate ions, and organoperoxide. A high quality dense fine-grained conversion coating is formed, without a conventional titanium phosphate sol "conditioning" treatment being needed before phosphating.

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Description**COMPOSITION AND PROCESS FOR SIMULTANEOUSLY CLEANING AND  
CONVERSION COATING METAL SURFACES**Technical Field

This invention relates to a surface treatment method that simultaneously cleans and conversion coats metal surfaces and is applicable to a variety of metals. More specifically, this invention relates to a simultaneous cleaning/conversion treatment method that is capable of simultaneously cleaning and conversion coating a metal surface bearing oil, grease, etc., with the uniform formation thereon of a fine and dense conversion coating.

Background Art

Zinc phosphate conversion treatments are currently in wide use as underpaint coating treatments for the purpose of improving the post-painting corrosion resistance and paint adherence of metals. This technology is effective even when the metal substrate is made of iron or is a composite that contains several types of materials.

Zinc phosphate conversion coatings are typically formed on various metals, for example, by executing the following steps in the given sequence:

- (1) alkaline degreasing
- (2) water rinse
- (3) conversion treatment
- (4) water rinse
- (5) drain and dry.

When this sequence is used to lay down an underpaint coating, a surface-conditioning treatment using a titanium colloid treatment composition (any liquid treatment composition alternatively being designated herein as a "bath" for brevity, even though it may be used by spraying or the like rather than or in addition to immersion) is run as a pretreatment to the conversion step (3) for the purpose of ultimately forming uniform, fine, and dense conversion coating crystals.

Surface conditioning with a titanium colloid treatment bath activates the surface of the metal substrate and thereby induces the deposition of fine-sized conversion coating crystals and accelerates the rate of conversion coating forma-

tion. The disparity in the rates of conversion coating formation becomes particularly significant at relatively lower treatment temperatures below 60 °C.

One problem with the above-described prior-art surface treatment technology is the large number of steps, which makes the overall process quite lengthy and thus necessitates large-scale treatment facilities and large amounts of space. Not only does the above-described surface treatment technology consist of five or six steps, but the alkaline degreasing and water rinse steps are frequently implemented as multi-step processes in order to improve the cleaning efficiency. This raises the facility costs even further and also reduces the productivity by necessitating a substantial amount of time for the substrate to pass through the entire treatment process.

A second problem with the above-described prior-art surface treatment technology originates with the large number of factors that must be managed. For example, the alkalinity (total alkalinity and free alkalinity) of the degreasing solution must be managed in the alkaline degreasing step, while the acid concentration (total acidity and free acidity) of the treatment bath must be managed in the conversion treatment step. A major operating burden is imposed when the factors that must be managed cover so broad a range. A large cost overhead is also generated since reagents are consumed in each individual step. Moreover, the main component in the surface-conditioning treatment agent is a titanium colloid dispersion, which does not have an entirely satisfactory timewise stability and as a result must be suitably managed and periodically discarded and renewed.

It could be conjectured that these two problems could be solved by running the steps from alkaline degreasing through conversion treatment as a single process through the use of a surfactant-containing zinc phosphate-based conversion treatment bath for the joint execution of degreasing and conversion. However, when the attempt is made to execute degreasing and conversion simultaneously, the conversion reactions begin sequentially from the regions of the metal substrate that have been cleaned. This creates a pronounced tendency for the quality and appearance of the resulting conversion coating to be nonuniform.

In another approach, the surface-conditioning agent could be added to the

conversion treatment bath in anticipation of generating a surface-conditioning activity on the metal substrate during treatment by the conversion treatment bath. However, the titanium colloid main component is unstable in the acidic region and a surface-conditioning activity therefrom absolutely cannot be expected. Accordingly, even when the surface-conditioning agent is used in conjunction with the conversion treatment bath, fine-size coating crystals are not produced and in fact, due to a slow rate of film deposition, the nonuniformity in conversion film appearance ends up being even further emphasized.

Thus, as described above, there is fairly strong demand for a shortening of the current treatment sequence in order thereby to reduce facility costs, reduce reagent costs, and simplify treatment bath management. However, this demand remains unmet at present due to the substantial technical difficulties that must be surmounted in order to satisfy this demand.

#### Disclosure of the Invention

##### Problems to Be Solved by the Invention

The present invention was developed in order to solve the problems described above for the prior art. This invention introduces a method for treating metal surfaces that shortens the zinc phosphate conversion treatment sequence of alkaline degreasing - water rinse - (surface conditioning) - conversion treatment - water rinse - drain/dry by running the steps from alkaline degreasing to conversion treatment as a single step, that is, as a joint degreasing/conversion. In specific terms, the present invention introduces a method for simultaneously cleaning and conversion coating the surfaces of various metals that—by treatment of a particular oil-bearing metal surface with a single treatment bath in a single step—is able to simultaneously clean the metal surface and form thereon a uniform, fine, and dense conversion coating.

##### Summary of the Invention

It has been found that the addition of a heretofore unexamined organic oxidizing agent, namely, organoperoxide, to the conversion treatment bath made possible cleaning of the metal surface and the deposition of uniform, fine, and dense coating crystals due to the ability of the surfactant to clean the metal surface and the ability of the organoperoxide to accelerate the conversion coating

formation reactions.

In specific terms, then, the treatment method according to the present invention for simultaneously cleaning and conversion coating metal surfaces is characterized by the simultaneous execution of cleaning and conversion coating on a metal surface bearing oil, grease, etc., by contacting the said surface with a zinc phosphate-based cleaning and conversion treatment bath that comprises, preferably consists essentially of, or more preferably consists of, water, zinc ions, phosphate ions, surfactant, and organoperoxide. Such a bath constitutes a composition according to the invention.

#### Detailed Description of the Invention, Including Preferred Embodiments

The organoperoxide concentration in the aforesaid conversion treatment bath is preferably 50 to 1,500 parts per million by weight (hereinafter usually abbreviated as "ppm") and, independently, the surfactant concentration is preferably 0.5 to 5 grams per liter (hereinafter usually abbreviated as "g/L").

No particular restrictions apply to the type, shape, or dimensions of metals that may be treated by the method according to the present invention. For example, the method according to the present invention can be applied to a variety of iron and steel materials, for example, steel sheet and zinciferous metal-plated steel sheet, and to a variety of aluminum materials, for example, aluminum sheet and aluminum alloys such as aluminum-magnesium alloys and aluminum-silicon alloys. The method according to the present invention is applied to metals whose surface has picked up oil, grease, and the like. The nature of this adhering material is not critical, and it includes such oils and greases as rust-preventing oils, press oils, and the like. The adhering material may also contain admixed dust, iron powder, and other contaminants. Nor is the amount of adhering material a critical factor.

The zinc phosphate cleaning/conversion treatment bath employed by the method according to the present invention is essentially an acidic aqueous solution that contains zinc ions, phosphate ions, surfactant, and organoperoxide. The zinc ions concentration in this cleaning/conversion treatment bath is generally preferably from 0.5 to 5.0 g/L. An adequate coating weight may not be obtained when the zinc ions concentration is below 0.5 g/L; this leads to a decline

in the coverage ratio by the resulting conversion coating on the metal surface and thereby to an inadequate post-painting corrosion resistance. Concentrations in excess of 5.0 g/L can cause a coarsening of the coating crystals and can cause the resulting conversion film to be nonuniform, thereby producing in particular a decline in the post-painting paint film adherence.

The phosphate ions concentration in the cleaning/conversion treatment bath used by the method according to the present invention is preferably from 5.0 to 30.0 g/L. Concentrations below 5.0 g/L can make it difficult to form normal conversion coatings, while concentrations in excess of 30.0 g/L do not provide any additional increments in activity and are therefore uneconomical. The phosphate ions can be generated by the addition of phosphoric acid or its aqueous solutions to the conversion treatment bath or by the dissolution of sodium phosphate, magnesium phosphate, zinc phosphate, or the like in the conversion treatment bath. The stoichiometric equivalent as phosphate ions of any of these materials added to the bath is to be understood as part of the phosphate ions content of the bath, irrespective of the actual degree of ionization that exists in the bath. Also, although usually less preferred because of their higher cost, condensed phosphoric acids and their salts can be used as the source of phosphate ions and are to be understood as providing their stoichiometric equivalent as phosphate ions to the bath, irrespective of their actual degree of ionization and/or other dissociation.

A characteristic feature of the surface treatment method according to the present invention is that it simultaneously executes degreasing and conversion treatment. Surfactant is added to the subject cleaning/conversion treatment bath as the treatment component that exercises this degreasing activity. Surfactants usable by the method according to the present invention are selected from the group consisting of nonionic, cationic, anionic, and amphoteric surfactants, wherein, however, the combination of cationic surfactant with anionic surfactant must be avoided because it produces problems with treatment bath stability.

Nonionic surfactants for use in the method according to the present invention are exemplified by polyethylene glycol-type nonionic surfactants such as polyoxyethylene alkylphenyl ethers, polyoxyethylene alkyl ethers, polyoxyeth-

ylene fatty acid esters, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene-polyoxypropylene block polymers, and the like; polyhydric alcohol-type nonionic surfactants such as sorbitan fatty acid esters and the like; and amide-type nonionic surfactants such as fatty acid alkyl amides and the like.

5 Cationic surfactants for use in the method according to the present invention are exemplified by amine salt cationic surfactants such as higher alkylamine salts, polyoxyethylene higher alkylamines, and the like, and by quaternary ammonium salt cationic surfactants such as alkyltrimethylammonium salts. Ampho-  
10 teric surfactants for use in the method according to the present invention are exemplified by amino acid amphoteric surfactants such as methyl alkylaminopropionate and the like and betaine amphoteric surfactants such as alkyl dimethylbetaine and the like.

In regard to anionic surfactants for use in the method according to the present invention, their addition and use is in many cases impaired by their typically low solubility in acidic media. However, ethylene oxide adducts, such as the  
15 higher alkyl ether sulfate esters, can be added and utilized because they retain a good solubility even in acidic media. The preceding surfactants are suitably added to the cleaning/conversion treatment bath in the method according to the present invention in a concentration of approximately 0.5 to 5 g/L. However, the  
20 surfactant type and concentration should be selected as appropriate as a function of the particular type and concentration (pick up) of the oil or grease component that is to be cleaned off.

The cleaning/conversion treatment bath used in the present invention contains organoperoxide. The organoperoxide has an oxidizing function and also  
25 functions to induce fine-size crystal formation in the conversion coating. It is precisely the functions exercised by the organoperoxide that enable the surface treatment method according to the present invention to bring about cleaning and to form a uniform, fine, and dense conversion coating in the absence of a titanium colloid surface-conditioning treatment. The use of an organoperoxide-containing cleaning/conversion treatment bath is the most characteristic feature of  
30 the method according to the present invention.

The organoperoxide used in the subject conversion treatment bath is ex-

emplified by organoperoxides that have a simple peroxy moiety, such as tert-butyl hydroperoxide, di-tert-butyl peroxide, acetylacetone peroxide, cumene hydroperoxide, tert-butylperoxymaleic acid, and the like, and by organoperoxides that have a percarboxylic acid moiety, such as peracetic acid, monoperoxphthalic acid, persuccinic acid, and the like.

The organoperoxide is preferably added to give a concentration from 50 to 1,500 ppm in the cleaning/conversion treatment bath. An organoperoxide concentration in the conversion treatment bath below 50 ppm can result in an inadequate acceleration of conversion coating formation and inadequate results in terms of producing fine-size crystals in the coating. Concentrations in excess of 1,500 ppm do not produce any additional increments in results and are therefore uneconomical. When the organoperoxide has a low solubility in the treatment bath, it can be solubilized by the addition of a relatively small amount of a water-soluble organic solvent and this can be added to the conversion treatment bath.

The organoperoxide functions as an oxidizing agent in the cleaning/conversion treatment bath according to the present invention, and its decomposition products will therefore accumulate in the treatment bath. For example, alcohols are produced from hydroperoxides, alcohols and carboxylic acids are produced from peroxy esters, and carboxylic acids are produced from percarboxylic acids. The accumulation of these decomposition products does not attenuate the effects from the method according to the present invention. Accordingly, the presence of these organoperoxide decomposition products in the cleaning/conversion treatment baths according to the present invention from the beginning is unproblematic.

The zinc phosphate cleaning/conversion treatment bath used by the present invention may also contain etchant for the purpose of generating a uniform etch of the surface of the metal being treated. When the invention method is used to provide an underpaint coating on the metal surface, the cleaning/conversion treatment bath according to the present invention may also contain non-zinc divalent metal cations for the purpose of generating additional improvements in the painting performance.

Fluoride ions or complex fluoride ions, e.g., fluosilicate ions, can be used

as the etchant. Fluorine compounds that produce these ions are exemplified by hydrofluoric acid, fluosilicic acid, and their metal salts (sodium salt, potassium salt), and the etching ion is produced by the dissolution of these compounds in the conversion treatment bath. The etching ion is preferably present in the conversion treatment bath at a concentration from 200 to 2,000 ppm.

Nickel ions, manganese ions, cobalt ions, magnesium ions, calcium ions, and the like can be employed as the non-zinc metal ions additive. Each of these types of ions can be provided by dissolution in the conversion treatment bath of an oxide, hydroxide, carbonate, sulfate, phosphate, and/or the like of the corresponding metal. Added metal ions are preferably present in the conversion treatment bath at a concentration from 200 to 3,000 ppm.

Approximately 10 to 50 ppm of trivalent iron ions will accumulate in the treatment bath when a ferrous material such as steel sheet, etc., is being treated, but this will not attenuate the effects of the present invention. Accordingly, trivalent iron ions can be unproblematically present in the aforesaid concentration range in the cleaning/conversion treatment bath according to the present invention from the very beginning.

Because the cleaning/conversion surface treatment method according to the present invention simultaneously effects degreasing and conversion treatment in a single step, the admixture and accumulation of a grease/oil fraction in the treatment bath cannot be avoided during continuous treatment processes. The permissible concentration of the oil/grease fraction in the cleaning/conversion treatment bath is in general approximately 10 g/L, although this will vary as a function of the type and concentration of the surfactant.

The cleaning/conversion treatment bath used by the present invention need not contain nitric acid, nitrous acid, an organic nitro compound, etc., and in consequence thereof can be formulated as a treatment bath that is completely free of nitrogenous compounds. This nitrogen-free formulation eliminates the need for a nitrogenous compound treatment step during effluent treatment; this makes it quite easy for the surface treatment method according to the present invention to accommodate environmental regulations on the effluent levels of nitrogenous compounds.

The standard treatment sequence in the surface treatment method according to the present invention will consist of the cleaning/conversion treatment step followed by a water rinse and drain/dry steps. The water rinse can be implemented as a single-step or multistep process. The final water rinse is preferably a deionized water rinse. The drain/dry step is not necessarily executed when the metal surface will be painted, for example, by electrodeposition, after treatment by the method according to the present invention. Factors such as the drain/dry temperature and time are not crucial, and drying may be conducted with heating or at ambient temperature.

Zinc phosphate conversion treatment using the surface treatment method according to the present invention is ordinarily run by immersion or spraying or a combination thereof. In practice a satisfactory conversion film can be formed using treatment times (contact time between the metal surface and cleaning/conversion treatment bath) from approximately 1 minute to approximately 10 minutes. The temperature of the cleaning/conversion treatment bath is preferably 30 °C to 55 °C during its contact with the metal surface being treated.

When the metal workpiece is ferriferous, the organoperoxide used in the method according to the present invention also oxidizes dissolved divalent iron ions to trivalent iron ions, just as do the prior-art inorganic oxidizing agents. This prevents the accumulation of divalent iron ions, which is detrimental to the conversion reactions. Almost all of the trivalent iron ions afforded by oxidation react with the phosphate ion present in the conversion treatment bath to form an iron phosphate ( $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ ) sludge that is easily removed from the system.

The effects of the present invention will be illustrated below using working examples and comparative examples of actual treatments; however, the present invention is in no way limited by the following examples.

#### Examples

The test materials were cold-rolled steel sheet (SPCC-SD, sheet thickness: 0.8 mm), zinc-electroplated steel sheet (sheet thickness: 0.8 mm; plating weight: both surfaces 30 g/m<sup>2</sup>), galvanized hot-dip zinc-plated steel sheet (sheet thickness: 2.8 mm, plating weight: both surfaces 45 g/m<sup>2</sup>), and aluminum-magnesium alloy sheet (JIS-A5052, sheet thickness: 1.0 mm). In each case the

sheets were cut to 70 x 150 mm to prepare the specimens that were then subjected to the treatments in the working and comparative examples. Each test material was coated with 2 g/m<sup>2</sup> of a commercial cleaning/rust-preventing oil (NOX-RUST™ 550 from Parker Kosan Kabushiki Kaisha).

The treatment processes common to the working and comparative examples are given below.

(1) cleaning/conversion treatment

(The specific conditions are given in the respective working and comparative examples.)

(2) tap-water rinse

ambient temperature, 30 seconds, spray

(3) deionized water rinse

(deionized water with a conductivity of 0.2 microSiemens/cm)

ambient temperature, 20 seconds, spray

(4) drain/dry: hot air at 110 °C, 180 seconds

Each of the cleaning/conversion treatment baths used in the working and comparative examples was adjusted to the specified free acidity using sodium hydroxide unless specified otherwise. The free acidity (in points) of the treatment baths was the number of milliliters of titrant required until the color change from yellow to blue when a 10 mL sample of the treatment bath was titrated to the color change from yellow to blue with 0.1 N aqueous sodium hydroxide using Bromophenol Blue as the indicator.

The conversion coating weight was measured as follows. The mass of the treated sheet after the cleaning/conversion treatment was measured to give a value in grams denoted as "W1". The coating was then stripped off the treated sheet using the stripping solution and stripping conditions given below, and the mass in grams of the stripped sheet was measured to give a value denoted as "W2". The coating weight was then calculated from the following equation:

$$\text{coating weight in grams per square meter ("g/m}^2\text{")} = (W1 - W2)/0.021.$$

Stripping conditions

(1) For the cold-rolled steel sheet

stripping solution: 5 % aqueous chromic acid

stripping conditions: 75 °C, 15 minutes, immersion stripping.

(2) For the zinc-plated sheet

stripping solution: 2 weight % of ammonium dichromate + 49 weight % of 28 % aqueous ammonia + 49 weight % of pure water.

5 stripping conditions: room temperature, 15 minutes, immersion stripping.

(3) For the aluminum alloy sheet

stripping solution: 5 % aqueous chromic acid

stripping conditions: room temperature, 5 minutes, immersion stripping.

The deposited coating crystals were inspected with a scanning electron  
10 microscope (hereinafter usually abbreviated as "SEM") at 1,000× magnification. This magnified image was used to evaluate basis metal coverage (presence/absence of exposed substrate) and to measure the particle size of the conversion coating crystals for evaluation of fine-size crystal formation.

The following standards were used for reporting the basis metal coverage  
15 and the fine-size crystal formation:

(1) Standard for evaluation of crystal particle size

- + + less than 30 micrometers (good)
- + at least 30 micrometers but less than 50 micrometers (moderately poor)
- x at least 50 micrometers (poor)

20 (2) Standard for evaluation of basis metal coverage

- + + absolutely no exposure of basis metal detected (good)
- + moderate exposure of basis metal detected (moderately poor)
- x basis metal completely exposed (poor)

EXAMPLE 1

25 The cleaning/conversion treatment bath specified below was heated to 45 °C and used to treat cold-rolled steel sheet by immersion for 180 seconds. The resulting coating weight was 1.2 g/m<sup>2</sup>, and the fine-size crystal formation and basis metal coverage were both evaluated as good.

Conversion Treatment Bath

30 phosphate ions : 15 g/L (from addition of 75% phosphoric acid)  
zinc ions : 1.3 g/L (from addition of zinc oxide)  
nickel ions : 0.5 g/L (from addition of nickel carbonate)

fluorine component : 1.0 g/L (from addition of sodium fluosilicate)  
organoperoxide : 500 ppm (addition of t-butyl hydroperoxide)  
tert-butanol : 4.0 g/L  
surfactant : 1.0 g/L

5 (The surfactant was a polyoxyethylene-polyoxypropylene block copolymer with an average molecular weight of 10,000 and an ethylene oxide addition proportion of 80 %.)

oil component : 2.0 g/L (from addition of NOX-RUST™ 550)  
free acidity : 0.6 points

10

#### EXAMPLE 2

The cleaning/conversion treatment bath of Example 1 was used to treat zinc-electroplated steel sheet by immersion for 180 seconds. The resulting coating weight was 3.5 g/m<sup>2</sup>, and the fine-size crystal formation and basis metal coverage were both evaluated as good.

15

#### EXAMPLE 3

The cleaning/conversion treatment bath specified below was heated to 40 °C and used to treat cold-rolled steel sheet by spraying for 120 seconds. The resulting coating weight was 1.2 g/m<sup>2</sup>, and the fine-size crystal formation and basis metal coverage were both evaluated as good.

20

#### Conversion Treatment Bath

phosphate ions : 14 g/L (from addition of 75 % phosphoric acid)  
zinc ions : 1.3 g/L (from addition of zinc oxide)  
cobalt ions : 0.5 g/L (from addition of basic cobalt carbonate)  
organoperoxide : 1000 ppm (from addition of di-tert-butyl peroxide)  
25 tert-butanol : 2.0 g/L  
first surfactant : 1.0 g/L

(The first surfactant was polyoxyethylene sorbitan monolaurate with an average of 20 moles of ethylene oxide (hereinafter usually abbreviated as "EO") per mole of sorbitan.)

30

second surfactant : 0.5 g/L

(The second surfactant was a salt of a partial ester of sulfuric acid with an adduct between lauryl alcohol and ethylene oxide, with an average of 3 moles of EO per

mole of lauryl alcohol.)

oil component : 3.0 g/L (addition of NOX-RUST™ 550)

free acidity : 0.5 points

#### EXAMPLE 4

5           The cleaning/conversion treatment bath of Example 3 was used to treat galvanized hot-dip zinc-plated steel sheet by spraying for 120 seconds. The resulting coating weight was 3.3 g/m<sup>2</sup>, and the fine-size crystal formation and basis metal coverage were both evaluated as good.

#### EXAMPLE 5

10           The cleaning/conversion treatment bath specified below was heated to 43 °C and used to treat cold-rolled steel sheet by spraying for 30 seconds and then immersion for 90 seconds. The resulting coating weight was 1.3 g/m<sup>2</sup>, and the fine-size crystal formation and basis metal coverage were both evaluated as good.

#### Conversion Treatment Bath

15           phosphate ions : 17 g/L (from addition of 75 % phosphoric acid)

zinc ions : 1.5 g/L (from addition of zinc oxide)

fluorine component : 0.4 g/L (from addition of sodium fluoride)

organoperoxide : 100 ppm (from addition of acetylacetone peroxide)

20           oil component : 2.0 g/L (addition of NOX-RUST™ 550)

first surfactant : 1.5 g/L

(The first surfactant was an ether alcohol corresponding to addition of an average of 7 moles of EO per mole of oleyl alcohol.)

second surfactant : 0.5 g/L

25           (The second surfactant was lauryldimethylbetaine.)

free acidity : 0.7 points

#### EXAMPLE 6

30           The conversion treatment bath of Example 5 was used to treat zinc-electroplated steel sheet by spraying for 30 seconds and then immersion for 90 seconds. The resulting coating weight was 3.6 g/m<sup>2</sup>, and the fine-size crystal formation and basis metal coverage were both evaluated as good.

#### EXAMPLE 7

The conversion treatment bath of Example 5 was used to treat the aluminum alloy sheet by spraying for 30 seconds and then immersion for 90 seconds. The resulting coating weight was 2.5 g/m<sup>2</sup>, and the fine-size crystal formation and basis metal coverage were both evaluated as good.

#### COMPARATIVE EXAMPLE 1

The conversion treatment bath specified below was heated to 45 °C and used to treat cold-rolled steel sheet by immersion for 180 seconds. Presumably because neither the organoperoxide nor the surfactant were added to this treatment bath, the oil component was not removed even upon completion of the treatment and coating deposition was completely absent.

##### Conversion Treatment Bath

phosphate ions	: 15 g/L (from addition of 75 % phosphoric acid)
zinc ions	: 1.3 g/L (from addition of zinc oxide)
nickel ions	: 0.5 g/L (from addition of nickel nitrate)
fluorine component	: 1.0 g/L (from addition of sodium fluosilicate)
nitrate ions	: 7.0 g/L (from addition of sodium nitrate)
nitrite ions	: 100 ppm (from addition of sodium nitrite)
oil component	: 2.0 g/L (addition of NOX-RUST™ 550)
free acidity	: 0.6 points.

#### COMPARATIVE EXAMPLE 2

The conversion treatment bath specified below was heated to 45 °C and used to treat galvanized hot-dip zinc-plated steel sheet by immersion for 180 seconds. The resulting coating weight was 5.3 g/m<sup>2</sup>, and the basis metal coverage was evaluated as good. However, presumably because no organoperoxide was present, the crystal particles were coarse and fine-size crystal formation was evaluated as poor.

##### Conversion Treatment Bath

phosphate ions	: 15 g/L (from addition of 75 % phosphoric acid)
zinc ions	: 1.3 g/L (from addition of zinc oxide)
nickel ions	: 0.5 g/L (from addition of nickel nitrate)
fluorine component	: 1.0 g/L (from addition of sodium fluosilicate)
nitrate ions	: 7.0 g/L (from addition of sodium nitrate)

nitrit ions : 100 ppm (from addition of sodium nitrite)

surfactant : 1.0 g/L

(The surfactant was a polyoxyethylene-polyoxypropylene block copolymer with an average molecular weight of 10,000 and an ethylene oxide addition proportion of 80%.)

oil component : 2.0 g/L (addition of NOX-RUST™ 550)

free acidity : 0.6 points

### COMPARATIVE EXAMPLE 3

The conversion treatment bath specified below was heated to 40 °C and used to treat cold-rolled steel sheet by spraying for 120 seconds. The resulting coating weight was 0.3 g/m<sup>2</sup>. However, presumably due to the absence of organoperoxide, the fine-size crystal formation and basis metal coverage were both evaluated as poor.

#### Conversion Treatment Bath

phosphate ions : 14 g/L (from addition of 75 % phosphoric acid)

zinc ions : 1.3 g/L (from addition of zinc oxide)

cobalt ions : 0.5 g/L (from addition of basic cobalt carbonate)

first surfactant : 1.0 g/L

(The first surfactant was polyoxyethylene sorbitan monolaurate with an average of 20 moles of ethylene oxide (hereinafter usually abbreviated as "EO") per mole of sorbitan.)

second surfactant : 0.5 g/L

(The second surfactant was a salt of a partial ester of sulfuric acid with an adduct between lauryl alcohol and ethylene oxide, with an average of 3 moles of EO per mole of lauryl alcohol.)

oil component : 3.0 g/L (from addition of NOX-RUST™ 550)

free acidity : 0.5 points

### COMPARATIVE EXAMPLE 4

The conversion treatment bath specified below was heated to 40 °C and used to treat cold-rolled steel sheet by spraying for 120 seconds. The resulting coating weight was 2.1 g/m<sup>2</sup>. However, presumably due to the absence of organoperoxide, the fine-size crystal formation was evaluated as poor and the basis

metal coverage was evaluated as moderately poor.

Conversion Treatment Bath

phosphate ions : 14 g/L (from addition of 75 % phosphoric acid)  
zinc ions : 1.3 g/L (from addition of zinc oxide)  
5 cobalt ions : 0.5 g/L (from addition of basic cobalt carbonate)  
chlorate ions : 1.5 g/L (from addition of sodium chlorate)  
first surfactant : 1.0 g/L

(The first surfactant was polyoxyethylene sorbitan monolaurate with an average of 20 moles of ethylene oxide (hereinafter usually abbreviated as "EO") per mole of sorbitan.)

10 second surfactant : 0.5 g/L

(The second surfactant was a salt of a partial ester of sulfuric acid with an adduct between lauryl alcohol and ethylene oxide, with an average of 3 moles of EO per mole of lauryl alcohol.)

15 oil component : 3.0 g/L (addition of NOX-RUST™ 550)  
free acidity : 0.5 points

COMPARATIVE EXAMPLE 5

The conversion treatment bath of Comparative Example 4 was used to treat the aluminum alloy sheet by spraying for 120 seconds. However, film deposition was entirely absent, presumably due to the absence of the organoperoxide.

In summary:

- Examples 1 to 7, which employed a surface treatment method according to the present invention, were able to clean even the surface of oil-coated metal while simultaneously depositing a uniform, fine, and dense zinc phosphate conversion coating.

- Comparative Example 1 involved treatment with a surfactant-free conversion treatment bath, and in contrast to the above results was unable to deposit a conversion film due to an inadequate removal of the oil/grease component. Comparative Example 3 involved treatment with an oxidizing agent-free treatment bath, while Comparative Examples 2, 4, and 5 involved treatment with organoperoxide-free baths that contained inorganic oxidizing agents. In these cases, the film crystals were coarse and a uniform, fine, and dense conversion

film was not obtained.

Benefits of the Invention

The cleaning/conversion treatment method according to the present invention is able in a single step to simultaneously effect degreasing and zinc  
5 phosphate conversion treatment on the oil/grease-bearing surface of metals. Moreover, it is able thereby to form a uniform, fine, and dense conversion coating. The merits accruing to the use of the cleaning/conversion treatment method according to the present invention can be expected to extend over a  
10 broad range, including, for example, a substantial abbreviation of the treatment sequence, simplification of the treatment facilities, space savings, increased productivity, a reduction in reagent costs, simplification of reagent management, and the like.

Claims

1. An aqueous liquid composition for simultaneously cleaning and conversion coating metal surfaces, said composition comprising water and:
  - (A) dissolved zinc ions;
  - 5 (B) dissolved phosphate ions;
  - (C) surfactant; and
  - (D) organoperoxide.
2. A composition according to claim 1, consisting essentially of water and:
  - (A) dissolved zinc ions;
  - 10 (B) dissolved phosphate ions;
  - (C) surfactant; and
  - (D) organoperoxide; and, optionally, one or more of the following:
  - (E) an etchant component;
  - (F) divalent metal cations other than zinc and ferrous ions; and
  - 15 (G) not more than 50 ppm of ferric ions.
3. A composition according to claim 2, wherein zinc ions are present in an amount from 0.5 to 5.0 g/L, phosphate ions are present in an amount from 5.0 to 30.0 g/L, organoperoxide is present in an amount from 50 to 1500 ppm, and surfactant is present in an amount from 0.5 to 5 g/L.
- 20 4. A composition according to claim 3, wherein anions containing fluorine are present in an amount corresponding to a stoichiometric equivalent of from 200 to 2000 ppm and divalent metal ions selected from the group consisting of nickel, manganese, cobalt, magnesium, and calcium in a total amount from 200 to 3000 ppm.
- 25 5. A process of simultaneously cleaning and conversion coating a metal surface soiled with oil or grease or both by contacting the metal surface with an aqueous liquid composition according to any one of claims 1 to 4 for a time sufficient to form a conversion coating on the metal surface.
6. A process according to claim 5, wherein the metal surface is contacted  
30 with said aqueous liquid composition for a time from 1 to 10 minutes during which time the temperature of the aqueous liquid composition is maintained within the range from 30 to 55 °C.